Renewable and Sustainable Energy Reviews 27 (2013) 445–452

Contents lists available at SciVerse ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

Biodiesel production from used cooking oil: A review

Carlos Daniel Mandolesi de Araújo*, Claudia Cristina de Andrade, Erika de Souza e Silva, Francisco Antonio Dupas

Center of Excellence in Energy Efficiency, Federal University of Itajubá, UNIFEI, Av. BPS, 1303, Pinheirinho, Itajubá, MG, 37500-093, Brazil

ARTICLE INFO

Article history:
Received 6 January 2013
Received in revised form
4 June 2013
Accepted 16 June 2013
Available online 1 August 2013

Keywords:
Biodiesel
Used cooking oil
Catalysis

ABSTRACT

This paper aims at the assessment of the methods of production of biodiesel from different types of used cooking oil. Researches into the productive chain of this type of biofuel were performed in Brazil while several scientific studies approaching processes of pretreatment and transesterification of waste cooking oil were analyzed with their possible variations: alkaline catalysis, acid catalysis, enzymatic catalysis and non-catalytic conversion techniques, highlighting the main advantages and disadvantages of each analyzed route. The use of alkaline catalysts in transesterification is the most common technique employed by the industry, being the KOH the most recommended catalyst for the reaction with waste cooking oil. When water and acidity contents are high, pretreatment techniques and other types of catalysts such as solid acids are recommended. Moreover, the economic benefits provided by used cooking oil were analyzed, indicating reductions of up to 45% of direct production costs compared to virgin oils, even with the additional costs of the pretreatment. Finally, the availability of raw materials was estimated, indicating that the used cooking oil would have potential to supply up to 13% of the demand for biodiesel in Brazil.

Contents

1. Introduction . . . 445
2. Overview of the biodiesel chain . . . 446
3. Biodiesel in Brazil . . . 446
4. Waste cooking oil: costs and availability. . . . 446
5. Pretreatment of cooking oil. . . . 448
6. Methods for the production of biodiesel from waste cooking oil . . . 448
    6.1. Alkaline catalysis . . . 448
    6.2. Acid catalysis . . . 449
    6.3. Enzymatic catalysis . . . 449
    6.4. Non-catalytic conversion techniques for transesterification . . . 450
7. Conclusions . . . 450
References . . . 450

1. Introduction

The probable scarcity of fossil fuels in the near future, combined with concerns over the consequences of dependency on this type of energy source, in terms of changes in the Earth's climate, has forced the world to find alternatives that are less harmful to the environment. Renewable energy sources, especially vegetable fuel, have appeared as an important alternative [1].

About 45% of the energy and 18% of fuels consumed in Brazil are renewable. All over the world, 86% of the energy comes from non-renewable energy sources. Pioneer in the use of biofuels, Brazil has reached a position longed for many countries in the search of renewable sources of energy as strategic alternatives to petroleum [2].

Biofuels are less pollutant than fossil fuels because they emit less harmful chemical substances during combustion and their

* Corresponding author. Tel.: +55 35 36227508.
E-mail address: cdaniel_br@yahoo.com.br (C.D. Mandolesi de Araújo).

1364-0321/$ - see front matter Crown Copyright © 2013 Published by Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.rser.2013.06.014

production processes tend to be cleaner. The use of ethanol is regarded as one of the main mechanisms to fight global warming, as it reduces the emission of carbon dioxide (CO_2). Part of the CO_2 emitted by ethanol-powered vehicles is reabsorbed by sugarcane plantations. This makes CO_2 emissions partially compensated. Comparing with petroleum-based diesel, biodiesel has considerable environmental advantages. Studies from the National Biodiesel Board (association representing the biodiesel industry in the United States) show that the biodiesel burning can emit, on average, 48% less carbon monoxide; 47% less particulate material (absorbed by lungs) and 67% less hydrocarbon [2].

A great economic challenge for the biodiesel commercialization is the high cost of pure vegetable oils, representing between 70% and 85% of the overall production cost of this energetic input [3]. Among the sources of feedstock for the biodiesel production are rapeseed, palm, sunflower, and soybean oils. However, their availability to be used in the biodiesel production is limited due to competition with edible oil markets and consequent price increase [4]. Moreover, biodiesel production from edible oil causes a negative impact in the environment, as it requires large amounts of available farmland [5]. Therefore, the search of new sources of biodiesel production is necessary, such as waste frying oil that can be acquired at no charge.

Such waste is generated in several locations, mainly when we consider urban areas with high consumption of refined vegetable oils. There are basically two possible destinations for waste frying oil: sewage systems, causing water pollution and encumbering its treatment, and processing equipment that can transform waste into a new product [6]. Considerable amounts of this waste are still disposed of incorrectly in most places, as fast food chains and restaurants have increased due to the growth of the Brazilian population [7].

Therefore, the use of this waste for the biodiesel production is a promising alternative as it combines economical aspects, due to the oil low cost of acquisition, with environmental preservation, as it prevents water sources contamination at the same time producing a less pollutant fuel.

This study is aimed at assessing the main technologies used for biodiesel production from different types of used cooking oil, highlighting the strong and weak points of each analyzed route.

2. Overview of the biodiesel chain

The designation biodiesel was first introduced in the United States in 1992 by the National Soy Diesel Development Board (currently National Biodiesel Board), pioneer in the commercialization of biodiesel in that country. Biodiesel can be used interchangeably with petroleum-based diesel due to its similar features. Moreover, it emits less toxic gases, it is renewable, biodegradable, non-toxic, and is essentially free of sulfur and aromatics [8].

In chemical terms, biodiesel is made up of methyl or ethyl esters of fatty acids that can be produced from different lipid sources, through transesterification, reaction with alcohol in the presence of a base, acid, enzyme or solid catalyst [9]. Nowadays esterification and transesterification reactions are the most commonly used to produce biodiesel. Any type of feedstock containing free fatty acids and/or triglycerides, such as vegetable oil and animal fat, can be converted into biodiesel. However, end products must comply with strict quality standards before being accepted as biodiesel (European Normalization (EN) 14214; American Standards for Testing Materials (ASTM) D6751) [10–14]. The most commonly commercialized feedstock is edible oil from soybean, rapeseed, palm, sunflower, coconut and linseed among others [15]. The main advantages of using biodiesel are its renewability, better-quality exhaust gas emissions, its biodegradability and the organic carbon present in it is photosynthetic in origin. It does not contribute to emissions of carbon dioxide to the atmosphere, and consequently, to the greenhouse effect. Biodiesel contributes to a reduction of the main emissions resulted from petroleum derivatives, with considerable exception to nitrogen oxides (NOx). Several studies have confirmed the increase of NO*x* emissions. Its attenuation has been suggested with the use of additives and engine modifications. In the case of sulfur oxides (SO*x*), as biodiesel do not contain sulfur, the emissions of these oxides are minimized with its use [16].

Emissions of greenhouse effect gases in combination with biodiesel have been evaluated in the last decade, in European conditions, considering the use of colza and soybean as feedstock and methyl esters as B10 and B20. The results suggest reductions from 40 to 60% in emissions corresponding to pure diesel [17].

3. Biodiesel in Brazil

In January 2008, the National Program for the Production and Use of Biodiesel established the addition of 2% of biodiesel to conventional diesel (B2). Motivated by future opportunities, the biodiesel production sector was extremely optimistic resulting in the idle capacity of most industries. As a consequence, the installed capacity for the production of biodiesel was sufficient to meet a demand equal to the B7 (7% of biodiesel added to conventional diesel). The capacity surplus resulted in fierce competition and in public bids, causing a drop in prices at levels detrimental to the production chain. Within the same period, the price of soybeans reached extremely high levels, due to its use as food and feedstock for fuels. This set of factors has caused negative effects, such as failure to deliver the volume sold in public bids by some biodiesel producers. On this account, the government decided to anticipate for July 2008, the increase of the blend percentage to 3% (B3), an anticipation of nearly 12 months, in order to achieve a better balance between demand and supply [18]. Currently, B5 blend is 5% biodiesel and 95% petroleum-based diesel.

Fig. 1 shows biodiesel production, compulsory demand and nominal capacity authorized in Brazil from 2005 to 2012.

Currently, there are 67 biodiesel production plants authorized by the ANP for operation in the country, corresponding to a total capacity of 21,397 m^3/day [19].

It is in a scenario of energetic sustainability that the country is searching for new alternatives for feedstock sources to produce biodiesel, aimed at the cost reduction of end products greatly dependent on soybean oils as shown in Fig. 2.

Algae produced naturally and some types of non-edible plant oils, such as *Jatropha curcas*, castor bean and palm, can play a considerable role in the supply of alternative feedstock. On the other hand, they require large available farmland [20].

4. Waste cooking oil: costs and availability.

Compared to petroleum-based diesel, the high cost of biodiesel is a major barrier to its commercialization. It costs approximately one and a half times that of petroleum-based diesel depending on feedstock oils [21,22].

A largely accepted strategy to reduce the cost of biodiesel is to minimize feedstock costs. The use of waste cooking oil for the production of biodiesel in spite of virgin oil has been an effective way of reducing feedstock costs, besides bringing substantial environmental benefits as it provides an alternative for the final disposal of the oil previously discharged of in the environment [7].

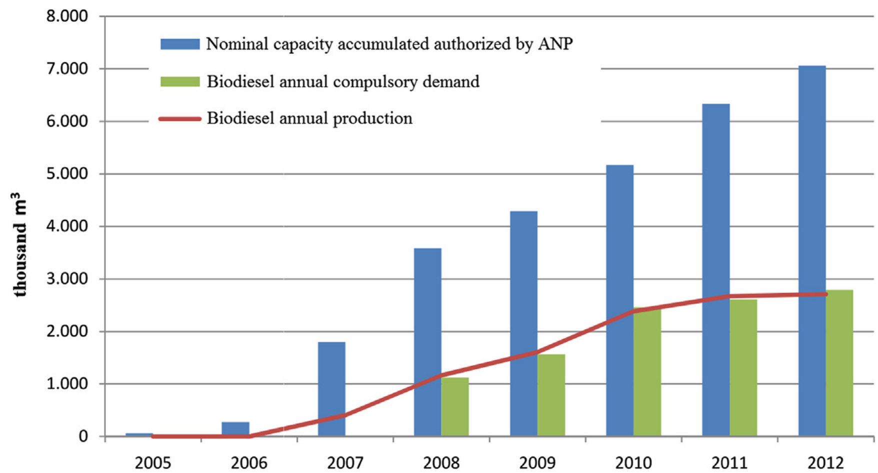


Fig. 1. Annual evolution of the nominal capacity allowed by the Brazilian National Petroleum Agency (ANP), biodiesel production and compulsory demand in Brazil [19].

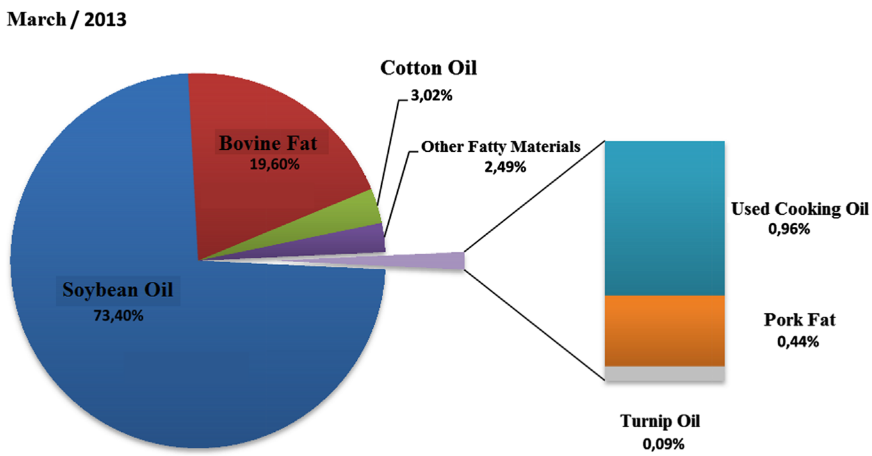


Fig. 2. Feedstock used to produce biodiesel [19].

Table 1
Average prices of selected oils used in biodiesel production in 2007 [23].

Oil	Price (US dollar/ton)
Crude palm oil	703
Rapesseed oil	824
Soybean oil	771
WCO	224
Yellow grease	412

According to Table 1, the cost of WCO is two and three times less than that of fresh vegetable oil, which leads to a significant reduction in the total processing cost.

In many countries, edible oils are used for frying and after variable time of use are disposed of. This type of oils differs from crude and refined oil. The presence of heat and water accelerates the hydrolysis of triglycerides, increasing the content of free fatty acids in the oil [24]. The content of free fatty acids and water has considerable negative effects upon the transesterification reaction [25]. They also interfere with the separation of biodiesel and glycerol. Most specifically, the oil viscosity increases considerably due to the formation of dimers and polymers in the used cooking oil. The molecular mass and the iodine value decrease, while the saponification value and the oil density increase [26–28]. Nowadays no methods for the systematic processing of waste oil from households are available; likewise, most of this waste is discharged in sewage systems, resulting in surface water pollution. In addition, more than 80% of the oil is consumed in households making its final disposal a heavy burden due to its high volume [29].

In Brazil, the consumption of vegetable oils per household is approximately 7 kg/year [30]. Assuming a maximum percentage loss of 18% due to the amount of oil absorbed by the food during frying [31] and that there are 57,320,555 households in the country [32], it is possible to arrive at an estimate of generation of used oils 329,020 t/year.

In the year 2012, 2,717,483 m^3 of biodiesel was produced in Brazil [33]. Taking into account the density of the biodiesel (0.877 kg/l at 25 °C) [34] and a yield of 94% in the production process most commonly used in industry (alkaline catalysis), it becomes possible to verify that the availability of waste cooking oil previously estimated would be able to supply up to 13% of annual demand for biodiesel in the country. It is worth noting that it was recorded only the amount of oil generated in households, excluding establishments and industries, fact that tends to contribute to increase the potential participation of used cooking oil in demand for biodiesel.

Technically, the methods for the production of biodiesel from used cooking oil do not differ from conventional transesterification processes using alkaline, acid and enzymatic catalysts. Depending on the undesirable components (especially free fatty acids and water), each catalyst have advantages and disadvantages. Therefore, taking the oil quality into account, a feedstock pretreatment phase might be needed with a view to comply with the quality standards required for the transesterification reaction.

Few studies in the literature talk about the additional costs inherent in the pretreatment step. However, it is possible to see a significant improvement in the economic viability of the process from residual oils compared to virgin oils [35], reaching a reduction of up to 45% of direct production costs, even with the additional costs of the pretreatment [36].

The following sections bring various experiments conducted for the oil pretreatment as well as different transesterification methods.

5. Pretreatment of cooking oil

Analysis could not detect considerable differences between used cooking oil and virgin oils [37]. Therefore, in most cases, heating and removal by filtration of solid particles are sufficient for the subsequent transesterification reaction. However, in some cases, outputs of the oil decomposition have deteriorated its quality, fact that can lead to a reduction of the ester performance and the formation of undesirable products during biodiesel production. The negative effects of the undesirable compounds can be avoided by a previous treatment of the used cooking oil. Different types of pretreatment have been used to this purpose, such as: steam injection, neutralization, vacuum evaporation and vacuum filtration [27].

Steam and methods of sedimentation were used to investigate the effects of pretreatment in the composition of used cooking oil and the esters produced from it. The study was performed in two steps with the oil heating at a temperature of 65 °C followed by sedimentation. The results of both pretreatment steps show that there was a reduction in the content of humidity and free fatty acids and a substantial reduction in viscosity, besides an increase in the calorific power. The pretreated oil was transesterified and the reduction of the acidity value (6.3–4.3%) and the humidity content (1.4–0.4%) responded for a substantial increase in ester performance (from 67.5% to 83.5%), as observed [38].

A series of pretreatment methods was used to reduce free fatty acids, water and polymers contents in used cooking oil before the two-step transesterification process was carried out being KOH the catalyst at 65 °C for 90 min. Free fatty acids were removed by neutralization and separated as soap while the high polymer content was treated with activated charcoal and removed by adsorption [39].

Other pretreatment methods have been reported in the literature: methods of filtration and drying by microwave oven at 60 °C for 10 min [40]; magnesium sulfate used as a drying agent followed by filtration under vacuum to remove any suspended matter and magnesium crystals [41]. Prior to the transesterification of used cooking oil a pretreatment by centrifugation was performed with a view to remove any solid matter. Water was removed by mixing the oil with 10% silica gel (28–200 mesh) followed by stirring and vacuum filtration [42]. Another experiment performed the waste cooking oil filtration under vacuum after dehydration over night using anhydrous sulfate followed by a new filtration under vacuum prior to the transesterification [43]. Biodiesel was produced from waste sunflower oil pretreated by drying over calcium chloride and filtration by cellulose filter in order to remove any suspended matter and calcium chloride crystals [44].

Although the removal of impurities such as water, free fatty acids and polymers prior to transesterification can improve used cooking oil ester performance and quality, pretreatments tend to increase biodiesel production costs suggesting a more in-depth analysis of the methods to be employed.

6. Methods for the production of biodiesel from waste cooking oil

6.1. Alkaline catalysis

The use of alkaline catalysts in the transesterification of waste cooking oil is the most commonly used technique by the industry; however, it has several limitations. The most commonly used catalysts are potassium hydroxide (KOH) and sodium hydroxide (NaOH) which are high sensitive to the purity of the reaction being affected by the water and free fatty acids contents [45,46]. The presence of water may cause the ester saponification under alkaline conditions. Moreover, the free fatty acids can also react with the alkaline catalyst producing soaps and water. The saponification does not only use up the catalyst, but also causes the formation of emulsions which impair the biodiesel separation, recuperation and purification. Therefore, dehydrated vegetable oil with free fatty acids content lower than 1%, anhydrous catalysts and anhydrous alcohol are essential for the commercial feasibility of alkaline catalyst systems. Nevertheless, several studies on the transesterification of waste cooking oil employing this type of catalyst can be found in the literature [7].

Several researchers have been using NaOH for the transesterification, in spite of its lengthy reaction ratio [27]. The use of methanol and NaOH as catalysts in the transesterification of used coconut oil with free fatty acids content of 1.47% was reported, being observed a maximum performance of 94% for the temperature range between 60 and 65 °C, catalyst concentration of 0.5% and twice the stoichiometric proportion of methanol [47]. Similarly, the transesterification of used cooking oil with acidity content in the range of 0.42–2.07 mg of KOH/g, using NaOH as catalyst was also reported [41]. Another experiment performed the transesterification with ethanol, using NaOH as catalyst, having temperature reaction of 60 °C for 20 min and catalyst optimum concentration of 0.08%. The average overall conversion was 94.5% [48]. The use of NaOH as catalyst in the transesterification of used cooking oil was also reported by [49–51].

Other studies have analyzed the use of KOH catalyst as the precursor of the transesterification reaction. Biodiesel was produced from the alkaline transesterification of used sunflower oil with low acidity value. The process was performed with methanol in the presence of KOH at 55 °C for 2 h [52]. Studies have been reported on the variables affecting the performance and features of the biodiesel produced from used cooking oil using KOH and NaOH as catalysts in two concentrations (0.5% and 1.0%), two reaction temperatures (25 and 65 °C) and three methanol/oil molar ratio values (3:1, 6:1 and 9:1), being the highest performances achieved with KOH. Results have shown the best performance percentage was obtained with methanol/oil molar ratio of 6:1, having KOH as the catalyst (concentration at 1%) at a temperature of 65 °C [53]. With the same catalyst, the transesterification of used cooking oil with acidity values ranging from 0.67 to 3.4 mg of KOH/g was performed with methanol, evidencing that the biodiesel best performance (88–90%) was achieved for a proportion of methanol/oil between 7.8 and 8.1 during 80–90 min at temperature ranging from 30–50 °C in the presence of 0.75 wt% KOH [54]. Another experiment used ethanol and KOH for the transesterification of used soybean oil. The reaction was performed at a constant temperature of 35 °C aimed at the minimization of the heating cost and ethanol evaporation [55]. The catalysts activities of NaOH and KOH were compared in the transesterification reaction of used cooking oil with acidity value of 2.76, concluding that the KOH provides higher reaction velocity than the NaOH [56]. Therefore, potassium hydroxide has been considered the best catalyst for the transesterification of waste edible oils [57].

6.2. Acid catalysis

As previously referred to, a drawback of the transesterification with alkaline catalyst is due to the process sensibility to the reagents purity, especially in terms of water and free fatty acid contents. Studies report that acid catalysts are insensitive to the acidity value and are better than alkaline catalysts for vegetable oils with acidity value higher than 1% [58].

Studies on the transesterification of edible oil using strong acids are available in the literature [59–62]. The transesterification of triglycerides can be usually catalyzed by inorganic acids such as sulfuric acid, hydrochloric acid, phosphoric acid and sulfonate organic acids. The transesterification by acid catalysis starts by mixing the oil directly with acidified alcohol, in a way that separation and transesterification can occur in a single step, being alcohol the esterification solvent and reagent [63]. The transesterification of used cooking oil from coffee shops with sulfuric acid and KOH was reported. Partially hydrogenated soybean oil and margarine were transesterified with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 2-ethoxyethanol. Ester performances were calculated when the product was put in sedimentation for 48 h at 25 °C, followed by matter removal by gravity and filtration. The filtered product was left to rest at 5 °C for 7 days and then filtered once again. Results have shown that acid catalysis performed better than alkaline reaction, except for methyl esters, despite the longer time-consuming process [64]. Pilot experiments carried out the transesterification of waste cooking oil in the presence of sulfuric acid at 70 °C. A minimum molar ratio of 50:1 to methanol/oil and acid concentration of 1.5–3.5% were used. The high methanol proportion was used to enable a high balance for the oil conversions into esters [65,66].

Catalysts activities of several acids for the transesterification of used cooking oil have been compared. The transesterification of waste palm oil was carried out under different conditions. Sulfuric and hydrochloric acid and ethanol were used in different concentrations. Catalysts in the range of 1.5–2.25 M yield biodiesel with lower specific weight in a much shorter reaction time than in lower concentrations. In comparison with HCl, H_2SO_4 showed superior catalytic activity. The use of alcohol in excess provided considerable reductions in the reaction time. Hence, in order to reduce reaction time, transesterification catalyzed by Bronsted acids demands higher concentration of catalysts and higher molar ratio [67].

Besides Bronsted acids, Lewis acids have also been used in the vegetable oil transesterification. A process was developed for the production of esters from feedstock with high contents of free fatty acids using calcium acetate and barium acetate as catalysts. Such catalysts do not promote soap formation with free fatty acids; however, molar ratios higher than 3:1 promote salt formations. Other limitations include high temperature (200–250 °C) and high pressure (400–600 psi) needed for the reaction. Moreover, barium compounds are toxic to humans [68].

Manganese acetate and stearate, plumb, zinc, cobalt and nickel were also tested in a 1:12 alcohol/oil molar ratio at a temperature of 200 °C for 200 min. The results show that stearate is better than acetate due to improved oil solubility, evidencing, also, better performance than Bronsted acids with lower concentration of catalysts and lower oil/alcohol molar ratio [69].

Lately, researches on biodiesel have focused on the use of solid acid catalysts known as heterogeneous catalysts. Sulfonic resins, such as Nafion NR50, sulfated zirconia and tungstated zirconia may catalyze transesterification reactions as effectively as sulfuric acid [70]. Studies report that the solid acid catalyst ideal to the transesterification of used cooking oil is expected to have features such as interconnected system of large pores, moderate and high concentrations of strong acids sites and hydrophobic surface [71]. Different types of solid acid catalysts, such as MoO_3/SiO_2, MoO_3/ZrO_2, WO_3/SiO_2–Al_2O_3, and zinc stearate supported on silica were synthesized and evaluated for the biodiesel production from waste cooking oil. Zinc stearate immobilized on silica gel (ZS/Si) was the most effective and stable heterogeneous catalyst. The catalyst was reused several times without any loss in the activity revealing a 98% esters performance [72].

The advantages of using solid acids catalysts are insensitivity to acidity value; esterification and transesterification may be carried out simultaneously; the catalyst is easy to be recovered; water washing biodiesel is unnecessary; generally high performance in esters; much lower catalyst requirements per tons of biodiesel produced than in other processes; and catalysts may be used for a longer period of time and are environmentally friendly. However, these systems operate under high temperature and pressure.

6.3. Enzymatic catalysis

Lately, there has been a growing interest in the use of enzymes, such as lipases, for the catalysis of oils to produce biodiesel. This type of transesterification has advantages upon chemical catalysts reactions as it avoids the generation of by-products, the product is easy to be recovered, reaction conditions are moderate (temperature from 35–45 °C) and the catalyst is recyclable [73]. It has been reported that enzymatic reactions are insensitive to acidity value and water content and may be used for the transesterification of used cooking oil [73,74].

Several types of lipases have been studied and selected as can be shown in the experiment with four specific species: *Mucor miehei* (Lipozyme IM60), *Candida antarctica* (SP435), *Geotrichum candidum* and *Pseudomonas cepacia* (PS30). They were employed as catalysts for the transesterification of olive oil, soybean oil and tallow. Reaction conditions developed for the tallow proved to be effective also for the transesterification of used cooking oil in terms of the following parameters: temperature at 45 °C; stirring speed of 200 rpm; enzymatic concentration ranging from 12 to 25% and reaction time between 4 and 8 h (for primary alcohols) and 16 h (for secondary alcohols). *M. miehei* was most efficient for the tallow transesterification using primary alcohols (95% conversion) whereas *C. antarctica* and *P. cepacia* were more efficient for the use of secondary alcohols (90% conversion) [75].

Another experiment studied the continuous transesterification of used cooking oil with ethanol using immobilized *Burkholderia cepacia* (IM BS-30) as the catalyst and a recirculating packed-column reactor. Effects of the flow rate, temperature, reaction time and reusability of the enzyme upon the product performance were analyzed. The optimum conditions for the obtainment of 96% performance in ester were, flow rate, 30 ml/min; temperature, 50 °C; molar ratio, 4:1 ethanol/oil and reaction time, 48 h [76]. It was also reported that organic solvent-free methanolysis does not give high conversions [77]. Another advantage of this method is that the acidity value and water have little or no effect upon the methanolysis efficiency and the immobilized biocatalyst may be reused [78]. Similarly, a three-step methanolysis was performed with used cooking oil and lipases. In the process, one-third of alcohol was fed at the beginning of the reaction, one-third 10 h after and the other third 24 h after the reaction had started, enabling to conclude that if the molar ratio is greater than 0.5, the product becomes alcohol-insoluble [79].

Other types of investigations were performed on the enzymatic conversion of waste oils using *Rhizopus oryzae* immobilized lipase focusing on the optimization of several process parameters such as molar ratio of methanol/oil, biocatalyst load, reaction temperature and water content. Results indicate that methanol/oil molar ratio of 4:1, immobilized lipase/oil of 30% and 40 °C were suitable under 1 atm pressure. Under optimum conditions the yield of methyl

ester was around 88–90%. The lipase irreversible inactivation was observed and a stepwise addition of methanol to reduce the inactivation of immobilized lipases was proposed as in the above experiments [80].

It was clear that immobilization has a considerable effect upon the lipase catalytic activity especially when feedstock with high acid value and water content is used for the transesterification. Moreover, the following advantages for the use of lipases can be mentioned [46].

– Possibility of regeneration and reuse of immobilized waste, as it can be left in the reactor if reactivity is kept low.
– Higher enzyme thermal stability due to its inactive state.
– Easier separation from the product.

Some disadvantages include,

– Loss of some initial activity due to the volume of oil molecule.
– Number of support enzymes is not uniform.
– Biocatalysts are more expensive than natural enzymes.

6.4. Non-catalytic conversion techniques for transesterification

Due to methanol weak potential and the oil miscibility, its conversion is a very slow reaction. The non-catalytic options are designed to overcome delays in the initial reaction time caused by the low solubility of alcohol in the triglyceride phase. An approach which is now commercialized consists in the use of a solvent soluble in methanol and oil. The result is a fast reaction, on the order of 5 to 10 min with no catalyst residues, in any phase. One of these cosolvents is the tetrahydrofuran, chosen, partially, due to its boiling point near that of methanol and the need of a very low operational temperature, around 30 °C. The BIOX, a patented production process, converts triglycerides and free fatty acids into a two-step continuous process at atmospheric pressure and ambient temperature, all in less than 90 min. Through the addition of a cosolvent, the free fatty acids are converted first, and next are the triglycerides without the need of any pretreatment phase. The process reaches a conversion higher than 99%, even when feedstock have high acid value (up to 10%), such as animal fat or crude palm oil. 99.9% of the cosolvent is recovered and the excess of methanol used in the process is then recycled and reused [81].

A second approach uses methanol at extremely high temperatures and high pressure. This process is known as supercritical methanol. The use of supercritical technology in the production of biodiesel is a forthcoming technology. The supercritical methanol does not work only as a solvent, but also as an acid catalyst [82]. The use of supercritical alcohol for the transesterification of pure vegetable oil is well-reported in the literature [83–88]. However, its application in the transesterification of used cooking oil is not yet well-documented. Some advantages of its application are [89,90],

– Glycerides and free fatty acids react with equivalent rates.
– The homogeneous phase eliminates diffusive problems.
– The process tolerates great percentages of water in the catalytic process of the feedstock requiring periodical removal of water or an intermediary phase to prevent catalyst deactivation.
– The catalyst removal phase is eliminated.
– If a high methanol/oil ratio is used, the total oil conversion can be achieved in few minutes.

Despite all the above mentioned advantages, the supercritical methanol method has serious disadvantages, such as:

– The process operates at extremely high pressures (25–40 MPa);
– The high temperatures (350–400 °C) result proportionally in high heating and cooling costs;
– High methanol: oil ratios (generally established at 42:1) involve high costs for the evaporation of the unreacted methanol;

7. Conclusions

Biodiesel as an alternative fuel to diesel engines has become more important due to the environmental impacts of petroleum-based diesel. The main challenges for the insertion of this biofuel in the market are its cost and availability of feedstock as fat and oils. Through the collection of different types of used cooking oils, the cost of biodiesel is considerably reduced and the negative impact of the waste oil disposal in the environment is minimized. However, in the frying process, the oil undergoes several reactions which lead to the formation of undesirable compounds such as polymers and free fatty acids, among others. This poses several challenges in the transesterification of used cooking oil, requiring an additional pretreatment step to remove these impurities. However, studies have shown a reduction of up to 45% of the direct cost of production, even with the additional costs of pretreatment.

An estimate of the availability of raw material was also prepared, concluding that the used cooking oil have the potential to supply up to 13% of the demand for biodiesel in Brazil and that the efforts may be focused not only on the subsidies and aspects of the productive process, but also in the quantification and monetization of direct and indirect environmental impacts caused by the disposal of waste cooking oil in the environment as a variable of the impact in the biofuel final price.

From the technical point of view, NaOH and KOH are the most largely used catalysts in the alkaline transesterification with KOH being the most suitable for the production of biodiesel from wastes such as cooking oil. If the content of free fatty acids is higher than 1%, an acid catalyst is a good choice. However, this process requires a high concentration of the catalyst and the molar ratio leading to corrosion problems. The most commonly used acids are sulfuric and sulfonic. Despite its operation under high pressure and temperature, the use of solid acids could be a better choice for the transesterification of used cooking oil with high acidity value.

In the conventional transesterification reaction, both methanol and ethanol can be used as esterification agents, being methanol the most commonly used. Few reports are available on the use of other alcohols. The use of enzymes has also been employed in the biodiesel production with reports of high performance in esters from used cooking oil; however, the long reaction time and the short activity period of the enzymes are also issues that affect its economical feasibility. In case of supercritical alcohol, higher reaction rates were observed when comparing with conventional transesterification. Other advantage of this process is that the free fatty acids are fully converted into esters. Nevertheless, requirements of high temperature and high pressure and the oil/alcohol molar ratio make the process expensive for industrial production.

References

[1] Santana GCS, Martins PF, Silva NL, Batistella CB, Filho RM, Maciel MRW. Simulation and cost estimate for biodiesel production using castor oil. Chemical Engineering Research and Design 2010;88:626–32.
[2] Agência Nacional Do Petróleo, Gás Natural e Biocombustíveis (ANP). Available from: 〈http://www.anp.gov.br/?pg=9201&m=&t1=&t2=&t3=&t4=&ar=&ps=&cachebust=1262617588151〉 (acessed March, 2012).
[3] Haas MJ, Foglia TA. Alternate feed stocks and technologies for biodiesel production. In: Knothe G, Krahl J, Gerpen JV, editors. Biodiesel Handbook 2005. Urbana, IL: AOCS Press; 2005. p. 42–61.

[4] Kansedo J, Lee KT, Bhatia S. Cerbera odollam (sea mango) oil as a promising non-edible feedstock for biodiesel production. Fuel 2009;88:1148–50.
[5] Ahmad AL, Yasin MNH, Derek CJC, Lim JK. Microalgae as a sustainable energy source for biodiesel production: a review. Renewable and Sustainable Energy Reviews 2011:584–96.
[6] Guabiroba, R.C., D'Agosto, M.A. Modelo de Cadeias de Coleta de Óleo Residual de Fritura para a Produção de Biodiesel Baseado em Cenários Nacional e Internacional", XXII ANPET, Fortaleza, CE, Brasil, 2008;.
[7] Enweremadu CC, Mbarawa MM. Technical aspects of production and analysis of biodiesel from used cooking oil—a review. Renewable and Sustainable Energy Reviews 2009:2205–24.
[8] Martini N, Shell JS. Plant Oils as Fuels—Present State of Science and Future Development. Berlin: Spinger; 276.
[9] Knothe G. What is biodiesel? In: Knothe G, Krahl J, Gerpen JV, editors. Biodiesel Handbook 2005. Champaign, IL: AOCS Press; 2005. p. 1–3.
[10] Ali Y, Hanna MA. Alternative diesel fuels from vegetable oils. Bioresource Technology 1994;50(2):153–63.
[11] Mittelbach M. Diesel fuel derived from vegetable oils. VI. Specifications and quality control of biodiesel. Bioresource Technology 1996;56(1):7–11.
[12] Altin R, Cetinkaya S, Yucesu HS. The potential of using vegetable oil fuels as fuel for diesel engines. Energy Convers Manage 2001;42(5):529–38.
[13] Canakci M, Sanli H. Biodiesel production from various feedstocks and their effects on the fuel properties. Journal of Industrial Microbiology and Biotechnology 2008;35(5):431–41.
[14] Hossain AK, Davies PA. Plant oils as fuels for compression ignition engines: a technical review and life-cycle analysis. Renewable Energy 2010;1(1–13):135 2010;1(1–13):1.
[15] Keorbitz W. Biodiesel production in Europe and North American, an encouraging prospect. Renewable Energy 1999;16:1078–83.
[16] U.S. EPA, "A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions" Draft Technical Report, October 2002. 〈http://www.epa.gov/otaq/models/analysis/biodsl/p02001.pdf〉 (acessed March, 2012).
[17] IEA, Biofuels for transport: an international perspective, IEA/EET, Paris, May 2004.
[18] Vaccaro GLR. Prospective scenarios for the biodiesel chain of a Brazilian state. Renewable and Sustainable Energy Reviews 2010;13:1263–9.
[19] ANP, 2103. Boletim Mensal do Biodiesel, Abril de 2013. Available from: 〈http://www.anp.gov.br/?pg=65917&m=&t1=&t2=&t3=&t4=&ar=&ps=&cachebust=1370112188884〉 (acessed May 2013).
[20] Dorado MP. Raw Biofuels Refining and Performance 2008. New York: McGraw-Hill; 107–47.
[21] Lott M. Personal Communication. Lanham, MD: QSS Group Inc.; 20706.
[22] Prokop T. Personal Communication. Coachella, CA: Imperial Western Products; 2002.
[23] Demirbas A. Economic and environmental impacts of the liquid biofuels. Energy Education Science and Technology 2008:37–58.
[24] Marmesat S, Rodrıguez-Macado E, Velasco J, Dorbangarnes MC. Used frying fats and oils: comparison of rapid tests based on chemical and physical oil properties. International Journal of Food Science & Technology 2007;42:601–8.
[25] Canakci M, Ozsezen AN. Evaluating waste cooking oil as alternative diesel fuel. Gazi University Journal of Science 2005;18(1):81–91.
[26] Tomasevic AV, Siler-Marinkovic SS. Methanolysis of used frying oil. Fuel Processing Technology 2003;81:1–6.
[27] Kulkarni MG, Dalai AK. Waste cooking oil—an economical source for biodiesel: a review. Industrial & Engineering Chemistry Research 2006;45:2901–13.
[28] Ruiz-Mendes MV, Marmesat S, Liotta A, Dobarganes MC. Analysis of used frying fats for the production of biodiesel. Grasas y Aceites 2008;59(1):45–50.
[29] Alcantara R, Amores J, Canoira L, Fidalgo E, Franco MJ, Navarro A. Catalytic production of biodiesel from soy-bean oil, used frying oil and tallow. Biomass & Bioenergy 2000;18:515–27.
[30] IBGE, 2010. Pesquisa de Orçamentos Familiares 2008-2009: Aquisição Alimentar Domiciliar Per Capita, Available from: 〈http://www.ibge.gov.br/home/estatistica/populacao/condicaodevida/pof/2008_2009_analise_consumo/pofanalise_2008_2009.pdf〉 (acessed May 2013).
[31] Amorim MMA, Junqueira RG, Jokl L. Consumo de óleo e gordura nas preparações do almoço self-service. Alimentos e Nutrição, Araraquara 2010; v. 21(n. 2):217–23 abr./jun.
[32] IBGE, 2010. Censo Demográfico 2010. Available from: ftp://ftp.ibge.gov.br/Censos/Censo_Demografico_2010/Familias_e_Domicilios/Table1_2.pdf (acessed May 2013).
[33] ANP, 2013. Produção de biodiesel – B100 produtor – 2005/2013. Available from: 〈http://www.anp.gov.br/?dw=8740〉 (accessed May 2013).
[34] Santos RMG, Maia IS, Santos NAC, Amaral BA, Castro VD, Carvalho JRM, Biodiesel de soja—Prática experimental de transesterificação para as aulas de química orgânica. 29a Reunião Anual da Sociedade Brasileira de Química, 2006.
[35] Yaakob Z, Mohammad M, Alherbawi M, Alam Z, Sopian K. Overview of the production of biodiesel from waste cooking oil. Renewable and Sustainable Energy Reviews 2013;18:184–93.
[36] Zhang Y, Dubé MA, McLean DD, Kates M. Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis. Bioresource Technology 2003;90:229–40.
[37] Knothe G, Dunn RO, Bagby MO. Biodiesel: the use of vegetable oils and their derivatives as alternative diesel fuels. ACS symposium series no. 666: fuels and chemicals from biomass; 1997.p. 172–208.
[38] Supple B, Holward-Hildige R, Gonzalez-Gomez E, Leahy JJ. The effect of steam treating waste cooking oil on the yield of methyl ester. Journal of the American Oil Chemists' Society 2002;79(2):175–8.
[39] Cvengros J, Cvengrosova Z. Used frying oils and fats and their utilization in the production of methyl esters of high fatty acids. Biomass Bioenergy 2004;27:173–81.
[40] Saifuddin N, Chua KH. Production of ethyl ester (biodiesel) from used frying oil: optimization of transesterification process using microwave irradiation. Malaysian Journal of Chemistry 2004;6(1):77–82.
[41] Felizardo P, Correia MJN, Raposo I, Mendes JF, Berkemeier R, Bordado J. Production of biodiesel from waste frying oil. Waste Management 2006;26:487–94.
[42] Issariyakul T, Kulkarni MG, Dalai AK, Bakhshi NN. Production of biodiesel from waste fryer grease using mixed methanol/ethanol system. Fuel Processing Technology 2007;88:429–36.
[43] Dias JM, Alvim-Ferraz MCM, Almeida MF. Comparison of different homogeneous alkali catalysts during transesterification of waste and virgin oils and evaluation of biodiesel quality. Fuel 2008;87:3572–8.
[44] Predojevic ZJ. The production of biodiesel from waste frying oils: a comparison of different purification steps. Fuel 2008;87:3522–8.
[45] Zhang Y, Dube´ MA, McLean DD, Kates M. Biodiesel production from waste cooking oil. 1. Process design and technological assessment. Bioresource Technology 2003;89:1–16.
[46] Marchetti JM, Miguel VU, Errazu AF. Possible methods for biodiesel production. Renewable & Sustainable Energy Reviews 2007;11:1300–11.
[47] Arquiza AC, Bayungan MC, Tan R. Production of biodiesel and oleochemicals from used frying oil. Los Baños: University of Philippines; 2000.
[48] Chhetri AB, Watts KC, Islam MR. Waste cooking oil as an alternative feedstock for biodiesel production. Energies 2008;1:3–18.
[49] Leung YC, Chen GY. Biodiesel production using waste cooking oil from restaurant. Symposium on energy engineering in the 21st century (SEE2000), vol. 4; 2000. p. 1553–9.
[50] Leung DYC. Development of a clean biodiesel fuel in Hong Kong using recycled oil. Water Air, & Soil Pollution 2001;130:277–82.
[51] Guo Y, Leung YC, Koo CP. A clean biodiesel fuel produced from recycled oils and grease trap oils. Better air quality in Asian and Pacific rim cities, BAQ 2002. Hong Kong Polytechnic University; 16–18 December 2002. PS-55: 1–6.
[52] Rao GLN, Sampath S, Rajagopal K. Experimental studies on the combustion and emission characteristics of a diesel engine fuelled with used cooking oil methyl ester and its diesel blends. International Journal of Environmental Science and Technology 2007;4(2):64–70.
[53] Reefat AA, Attia NK, Sibak HA, El Sheltawy ST, El Diwani GI. Production optimization and quality assessment of biodiesel from waste vegetable oil. International Journal of Environmental Science and Technology 2008;5 (1):75–82.
[54] Phan AN, Phan TM. Biodiesel production from waste cooking oils. Fuel 2008;87:3490–6.
[55] Allawzi M, Kandah MI. Parametric study of biodiesel production from used soybean oil. European Journal of Lipid Science and Technology 2008;110 (8):760–7.
[56] Dorado MP, Ballesteros E, Mittelbach M, Lopez FJ. Kinetic parameters affecting the alkali-catalyzed transesterification process of used olive oil. Energy Fuels 2004;18:1457–62.
[57] Encinar JM, Gonzalez JF, Rodríguez-Reinares A. Biodiesel from used frying oil. Variables affecting the yields and characteristics of the biodiesel. Industrial & Engineering Chemistry Research 2005;44:5491–9.
[58] Freedman B, Pryde EH, Mounts TL. Variables affecting the yields of fatty esters from transesterified vegetable oils. Journal of the American Oil Chemists' Society 1984;61(10):1638–43.
[59] Schwab AW, Bagby MO, Freedman B. Preparation and properties of diesel fuels from vegetable oils. Fuel 1987;66(10):1372–8.
[60] Freedman B, Butterfield RO, Pryde EH. Transesterification kinetics of soybean oil. Journal of the American Oil Chemists' Society 1986;63(10):1375–80.
[61] Liu K. Preparation of fatty acid methyl esters for gas chromatography analysis of lipids in biological materials. Journal of the American Oil Chemists' Society 1994;71(11):1179–87.
[62] Canakci M, Gerpen JV. Biodiesel production via acid catalysis. Transactions of the ASAE 1999;42(5):1203–10.
[63] Cervero PJM, Coca J, Luque S. Production of biodiesel from vegetable oils. Grasas y Aceites 2008;59(1):76–83.
[64] Nye MJ, Williamson TW, Deshpande S, Schrader JH, Snively WH, Yurkewich TP, et al. Conversion of used frying oil to diesel fuel by transesterification: preliminary tests. Journal of the American Oil Chemists' Society 1983;60 (8):1598–601.
[65] Ripmeester WE. Modeling the production of biodiesel oil from waste cooking oil. B.A.Sc thesis, Department of Chemical Engineering, University of Ottawa;1998.
[66] McBride M. Modeling the production of biodiesel oil from waste frying oil. B.A. Sc thesis, Department of Chemical Engineering, University of Ottawa; 1999.
[67] Al-Widyan MI, Al-Shyoukh AO. Experimental evaluation of the transesterification of waste palm oil into biodisesl. Bioresource Technology 2002;85:253–6.
[68] Basu HN, Norris ME. Process for production of esters for use as a diesel fuel using a non-alkaline catalyst. US Patent no. 5525126, June 11, 1996.
[69] Di Serio M, Tesser R, Dimiccoli M, Cammarota F, Nasatasi M, Santacesaria E. Synthesis of biodiesel via homogeneous Lewis acid catalyst. Journal of Molecular Catalysis 2005;239:111–5.
[70] Dunford NT. Biodiesel production techniques. Food Technology Fact Sheet, FAPC-150; 2006. 〈www.fapc.biz〉 (acessed March 2012).
[71] Lotero E, Liu Y, Lopez DE, Suwannakarn K, Bruce DA, Godwin JG. Synthesis of biodiesel via acid catalysis. Industrial & Engineering Chemistry Research 2005;44:5353–63.

[72] Jacobson K, Gopinath R, Meher LC, Dalai AK. Solid acid catalyzed biodiesel production from waste cooking oil. Applied Catalysis B: Environmental 2008;85:86–91.
[73] Wu WH, Foglia TA, Marmer WN, Phillips JG. Optimizing production of ethyl esters of grease using 95% ethanol by response surface methodology. Journal of the American Oil Chemists' Society 1999;76(4):571–621.
[74] Hsu A, Jones KC, Marmer WN. Production of alkyl esters from tallow and grease using lipase immobilized in pyllosilicate sol–gel. Journal of the American Oil Chemists' Society 2001;78(6):585–8.
[75] Hsu A, Jones KC, Foglia TA, Marmer WN. Immobilized lipase-catalyzed production of alkyl esters of restaurant grease as biodiesel. Applied Biochemistry 2002;36(3):181–6.
[76] Hsu A, Jones KC, Foglia TA, Marmer WN. Continuous production of ethyl esters of grease using an immobilized lipase. Journal of the American Oil Chemists' Society 2004;81(8):749–52.
[77] Nelson LA, Foglia TA, Marmer WN. Lipase-catalyzed production of biodiesel. Journal of the American Oil Chemists' Society 1996;73(8):1191–4.
[78] Watanabe Y, Shimada Y, Sugihara A, Tominaga Y. Enzymatic conversion of waste edible oil to biodiesel fuel in a fixed-bed bioreactor. Journal of the American Oil Chemists' Society 2001;78(7):703–7.
[79] Shimada Y, Watanabe Y, Sugihara A, Tominaga Y. Enzymatic alcoholysis for biodiesel fuel production and application of the reaction to oil processing. Journal of Molecular Catalysis B: Enzymatic 2003;17:133–42.
[80] Chen G, Ying M, Li W. Enzymatic conversion of waste cooking oils into alternative fuel—biodiesel. Applied Biochemistry and Biotechnology 2006;129–132(1–3):911–21.
[81] BIOX Process, ⟨http://www.bioxcorp.com⟩ (acessed April 2012).
[82] Warabi Y, Kusdiana D, Saka S. Reactivity of triglycerides and fatty acids of rapeseed oil in supercritical alcohols. Bioresource Technology 2004;91:283–7.
[83] Saka S, Kusdiana D. Biodiesel fuel from rapeseed oil as prepared in supercritical methanol. Fuel 2001;80:225–31.
[84] Kusdiana D, Saka S. Kinetics of transesterification in rapeseed oil to biodiesel fuel as treated in supercritical methanol. Fuel 2001;80:693–8.
[85] Demirbas A. Biodiesel from vegetable oil in supercritical methanol. Energy Conversion and Management 2002;43:2349–56.
[86] Kusdiana D, Saka S. Effects of water on biodiesel fuel production by supercritical methanol treatment. Bioresource Technology 2004;91:289–95.
[87] Balat M. Biodiesel from vegetable oils via transesterification in supercritical ethanol. Energy Education Science and Technology 2005;16:45–52.
[88] Demirbas A. Biodiesel production via non-catalytic SCF method and biodiesel fuel characteristics. Energy Conversion and Management 2006;47:2271–82.
[89] Vera CR, D'Ippolito SA, Pieck CL, Parera JM. Production of biodiesel by two step supercritical reaction process with adsorption refining. In: 2nd Mercosur congress on chemical engineering and 4th Mercosur congress on process systems engineering (ENPROMER-2005); 2005.
[90] Balat M, Balat H. A critical review of bio-diesel as a vehicular fuel. Energy Conversion and Management 2008;49:2727–41.